TECHNICAL MEMORANDUM

TO: Dennis Crumpler / OAQPS

FROM: Eric Boswell / NAREL

COPY: Dr. Richard Tropp / DRI

AUTHOR: Steve Taylor / NAREL

DATE: September 14, 2005

SUBJECT: DRI Laboratory Audit

Introduction

On March 23, 2005, a Technical Systems Audit (TSA) was conducted at the Desert Research Institute (DRI) Division of Atmospheric Sciences Environmental Analysis Facility (EAF), located in Reno, NV. This TSA was conducted as part of the U.S. Environmental Protection Agency's (EPA) quality assurance oversight for the $PM_{2.5}$ Chemical Speciation Network, specifically, DRI's laboratory support for the Texas Commission on Environmental Quality (TCEQ). Recently, DRI has been contracted by TCEQ to analyze samples collected by the State of Texas for their $PM_{2.5}$ Chemical Speciation Network. The contract includes approximately twenty $PM_{2.5}$ Speciation sampling sites that require microgravimetric mass, ions, XRF, and carbon analysis using Speciation Trends Network (STN) analytical methods.

The EPA's quality assurance oversight for $PM_{2.5}$ speciation also includes oversight of the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network. Carbon analysis by the IMPROVE method was also an area of interest for this TSA because DRI performs all carbon analyses for samples collected by the IMPROVE network.

The EPA audit team consisted of Jewell Smiley and Steve Taylor from the National Air and Radiation Environmental Laboratory (NAREL) with Joann Rice and Dennis Crumpler from the Office of Air Quality Planning and Standards (OAQPS). This audit was a first annual inspection of DRI's laboratory systems and operations required for acceptable contract performance.

Summary of Audit Proceedings

The audit began with an introductory meeting with DRI senior staff and supervisors to present an overview of the audit process. Next on the agenda was a tour of the laboratory facility. Following the laboratory orientation the auditors proceeded to inspect specific areas of the laboratory to interview those technical staff who actually perform the analyses. At least one member of the DRI staff was always available to escort and assist the auditors. The following specific areas at the DRI facility were visited and inspected.

- ✓ Sample Receiving and Handling Laboratory - Brenda Cristani, Barbara Hinsvark
- ✓ Organic Carbon/Elemental Carbon (OC/EC) Laboratory - Dana Trimble, Antony Chen, Teresa Bohannan
- ✓ Ion Chromatography (IC) Laboratory - Barbara Hinsvark
- ✓ Gravimetric Laboratory - Brenda Cristani
- ✓ XRF Laboratory - Steven Kohl

Besides the areas mentioned above, interviews were also conducted with the following senior DRI staff.

- ✓ Dr. John Watson - Research Professor, DRI Quality Assurance Officer
- ✓ Dr. Judith Chow - Research Professor, DRI EAF Director
- ✓ Dr. Richard Tropp - Associate Research Professor, Project manager for TCEQ

DRI was initially contracted by TCEQ in 1999 to provide laboratory support for the Texas $PM_{2.5}$ Federal Reference Method (FRM) Program. The purpose of the FRM program is to determine if $PM_{2.5}$ mass concentrations are in compliance with the $PM_{2.5}$ national ambient air quality standards (NAAQS) for particulate matter (PM). DRI's support included microgravimetric analysis of $PM_{2.5}$ filters, logistical support such as shipping and receiving of filters, and data management support. The $PM_{2.5}$ chemical speciation network and the $PM_{2.5}$ STN was established by EPA in 2000 to characterize the chemical composition of $PM_{2.5}$. Nationally, there are approximately 180 non-trend supplemental speciation sites and 54 STN sites. DRI's laboratory support for the speciation program includes microgravimetric, carbon, ions, and elemental analyses as well as logistical and data management tasks. EPA awarded Research Triangle Institute (RTI) the national contract for providing laboratory support for all 54 STN sites and the majority of non-trend sites, however, for non-trend sites, states may choose a laboratory other than RTI. Initially, TCEQ contracted RTI for laboratory support for its $PM_{2.5}$ chemical speciation sites. Recently, in September/October 2004, a new contract was awarded by TCEQ for DRI to provide laboratory support for all supplemental $PM_{2.5}$ speciation sites in addition to the FRM sites. Texas currently has approximately twenty $PM_{2.5}$ FRM sites and twenty $PM_{2.5}$ non-trend chemical speciation sites that are supported by DRI. RTI continues to provide laboratory support for the 54 STN sites which include three sites in Texas.

DRI also provides carbon analysis support for the IMPROVE network. This support includes pre-treatment and analysis of 25 millimeter quartz-fiber filters for organic and elemental carbon (OC/EC) and the carbon sub-fractions using the IMPROVE thermal optical reflectance (TOR) method of analysis. DRI analyzes approximately 16,000 samples per year for the IMPROVE program.

A DRI led laboratory inter-comparison study between DRI and RTI is in progress. This special study will provide an additional quality assurance element for the transition of TCEQ's laboratory support from RTI to DRI. Both laboratories will analyze shared samples collected at special co-located Texas "test bed" sites in order to compare analysis results from both laboratories. STN analyses will include gravimetry, XRF, ions, and carbon. The study will also be a means for estimating precision of speciation data collected from the Rupprecht and Patashnick (R&P) non-trends samplers used in Texas. A third purpose of this study will be to test Gelman Teflon® filters and Pallflex quartz filters as an alternative to Whatman Teflon® and quartz filters that are routinely used to collect STN samples. DRI QA staff propose that changing to the alternate filters could provide better XRF detection limits using the thinner Gelman Teflon® filters and the ability to measure ions from the Pallflex quartz filters.

The EPA auditors were familiar with DRI's Quality Assurance Project Plan (QAPP) and pertinent SOPs. A few weeks before the TSA was scheduled, a set of single-blind Performance Evaluation (PE) samples was prepared at NAREL and submitted to DRI for analysis. Replicate sets of the PE samples were also analyzed by EPA as well as three other STN laboratories. At the time of the TSA most of the results from these PE samples were available to discuss with DRI staff. A Powerpoint presentation, delivered by Jewell Smiley to the DRI staff, allowed them to see how their laboratory compared in performance to the other participating laboratories. A detailed report of the PE study is in progress and is scheduled to be completed in the summer of 2005 (Reference 1).

Sample Receiving and Handling Laboratory

The sample receiving and handling laboratory was reviewed by all four members of the audit team. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOPs and documents.

- *DRI SOP #2-113.2 - $PM_{2.5}$ FRM Sample Shipping, Receiving, and Chain-of-Custody* (Reference 2)
- *DRI SOP #2-112.2 - $PM_{2.5}$ FRM Filter Pack Assembly, Disassembly, and Cleaning* (Reference 3)
- *Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods.* Quality Assurance Guidance Document 2.12. U.S. Environmental Protection Agency. Office of Research and Development, Research Triangle Park, NC. 1998. (Reference 4)

Barbara Hinsvark is the DRI logistics coordinator who is responsible for the coordination of field and laboratory operations. Brenda Cristani, DRI's weighing lab supervisor, was also available to demonstrate how samples for the Texas $PM_{2.5}$ program were processed and handled. Brenda, with the help of student assistants from the University of Nevada in Reno, demonstrated the process of shipping clean filters to the field sites and receiving the loaded filters back at the lab.

R&P Partisol-Plus Model 2025 Sequential Air Samplers are used by TCEQ to collect $PM_{2.5}$ air samples. For chemical speciation, samplers are paired at each site with one sampler loaded with Teflon® filters used for gravimetry, XRF, and ions analysis and one with quartz filters for carbon analysis. Nylon filters are not used by TCEQ in the R&P Model 2025 sampler. Working in a laminar flow hood, new pre-weighed Teflon® filters and pre-fired quartz filters are loaded into labeled cassettes and placed into protective containers. Barcodes and labels identifying the filter and cassette are placed on the protective containers. Sample identification and sampling date information are entered on field data sheets/chain of custody forms and also into a laboratory database. The assembled cassettes and protective containers are sealed into labeled plastic bags along with the field data sheets. The filters are sent to the field sites by second day delivery. After the sampling event, the loaded filters are returned to the laboratory by overnight delivery still mounted in the cassette, but are cooled to approximately 4 ^{O}C for preservation during transit. Upon receipt at the laboratory, the coolers are opened and the temperature is measured and recorded. Each cassette is disassembled, and the recovered filter is transferred to a petri slide. The bar code label is also transferred to the petri slide. The Teflon® filters are moved to the weighing room for equilibration and the quartz filters are stored under refrigeration until analysis. The filter holder cassettes are cleaned for reuse with de-ionized water using a dishwasher.

New filters are loaded into cassettes in the controlled conditions of the DRI laboratory to minimize sample contamination. In order to collect a sample, the cassette assemblies must be loaded into a magazine in the proper sequence which is then loaded into the air sampler. At present, speciation cassettes are loaded into the R&P sampler magazines at the Texas field laboratories. There is an increased potential for sample contamination and for the cassettes to be loaded out of sequence due to this extra handling. Cassettes could be loaded into magazines before shipping to the field if additional quality control becomes necessary.

Field blank data are routinely monitored to check for accidental contamination of the filter media. A summary report of field blank data were not available at the time of the TSA for the new DRI non-trends program. This data will be included in the DRI quality assurance report.

Good laboratory practices and compliance with EPA Regulatory requirements pertaining to $PM_{2.5}$ monitoring were observed for preparation of fresh cassettes to send to the field and for receiving the loaded filters from the field sites following sample collection. Documentation of each sample was also complete with each step of the process documented in an electronic database as well as on written forms. No deficiencies were noted for this area of laboratory operations.

Gravimetric Laboratory

Brenda Cristani, the weighing lab supervisor was interviewed for this part of the TSA. Lab technicians Heather Saunders and Cody Meredith were also available during the interview. The interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOPs and documents.

- *DRI SOP #2-114.2 - Gravimetric Analysis* (Reference 5)
- *Monitoring $PM_{2.5}$ in Ambient Air Using Designated Reference or Class I Equivalent Methods.* Quality Assurance Guidance Document 2.12. U.S. Environmental Protection Agency. Office of Research and Development, Research Triangle Park, NC. 1998. (Reference 4)

Mass determination typically proceeds by weighing the collection filter before and after the sampling event. The amount of Particulate Matter captured onto the surface of the filter can be calculated by a simple subtraction of the tare weight from the loaded filter weight. A Mettler Toledo MT5 microbalance is used for weighing the Texas filters. The DRI gravimetric measurements are performed in an environmentally controlled weighing room. The weighing room is configured to satisfy conditions of cleanliness, constant temperature, and constant humidity required by the program. Accurate control of the climate inside the weighing room is important because the balance calibration is very sensitive to temperature, and the equilibrated mass on a Teflon® filter is sensitive to humidity. The microbalance is also extremely sensitive to static electricity. DRI uses a custom made box containing several radioactive ^{210}Po radiation sources to dissipate static charge on filters. Each filter is placed into the box for 30 to 60 seconds just prior to being weighed. To satisfy requirements for cleanliness, the weighing room is kept under positive pressure with HEPA filtered air. To further reduce the potential for contamination, the microbalance is maintained under a laminar flow hood.

Two metallic mass standards were brought to the interview so that direct observations could be made as they were weighed. Both Ms. Cristiani and Ms. Saunders weighed the standards. Weighing results are presented in Table 1 and demonstrate excellent between lab agreement.

Table 1. Gravimetric Mass Determinations

Metallic Weight ID	NAREL Value (mg)	DRI Value (Brenda) (mg)	DRI Value (Heather) (mg)
M-100	100.000	99.999	99.999
M-200	200.004	200.003	200.004

The criteria for conditioning Teflon® filters used to collect $PM_{2.5}$ are specified in the EPA Quality Assurance Guidance Document 2.12 (Reference 4). The criteria specify a temperature between 20-23 ^{O}C, controlled to ± 2 ^{O}C for 24 hours. The average relative humidity (RH) must be between 30-40% controlled to ± 5% RH over 24 hours. DRI uses a digital hydrometer/thermometer to monitor the weighing room conditions. The temperature and humidity readings are automatically recorded into a database each minute. Dickson Temperature/Humidity data loggers were brought from NAREL to independently measure conditions inside of the weighing room. NAREL's data loggers were placed into the weighing room on the morning of the audit and remained there for several hours. Figure 1 shows a comparison of the temperature and humidity measurements inside the weighing room as recorded by NAREL and DRI data loggers. The average RH was 39.5 %

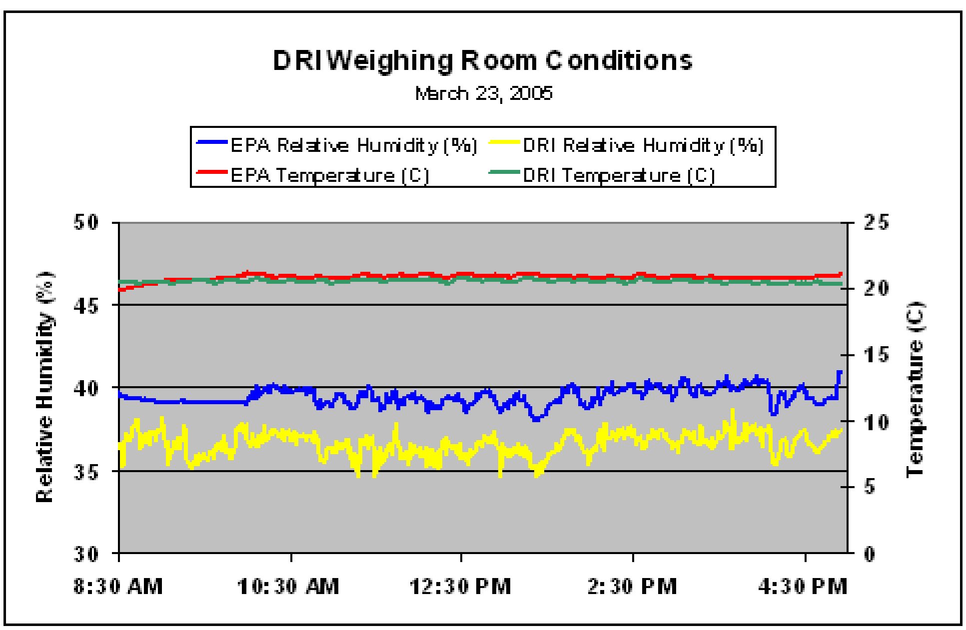

Figure 1

recorded by the NAREL device and 36.6 for the DRI device. The average temperature was 20.6 ^{O}C recorded by the NAREL device and 20.5 ^{O}C for the DRI device. The measurement differences are within acceptable limits based on the accuracy for each device. The data loggers have an expected accuracy of ± 2 % RH and ± 0.25 ^{O}C and and are traceable to the National Institute of Standards and Technology (NIST). The measurements indicate good humidity and temperature control of the weighing room for the time period indicated.

Results of a recent gravimetric PE study between NAREL and DRI were discussed with Ms. Cristiani. The study consisted of ten Teflon® filters and two metallic weights that were tared by both labs. Seven of the tared filters were used to collect air samples at NAREL and the remaining three filters served as blanks. All samples were equilibrated and weighed at NAREL prior to shipping cooled to DRI for their mass determinations.

Figures 2 and 3 summarize the results of the PE. Figure 2 presents the mass capture for each filter as determined by DRI and NAREL. Figure 3 presents the difference in captured mass determined by NAREL from the captured mass determined by DRI for all samples. The PE study showed excellent agreement between NAREL and DRI mass measurements with the largest capture difference of only 0.006 mg. A separate report for this PE study will be available at a later date (Reference 1).

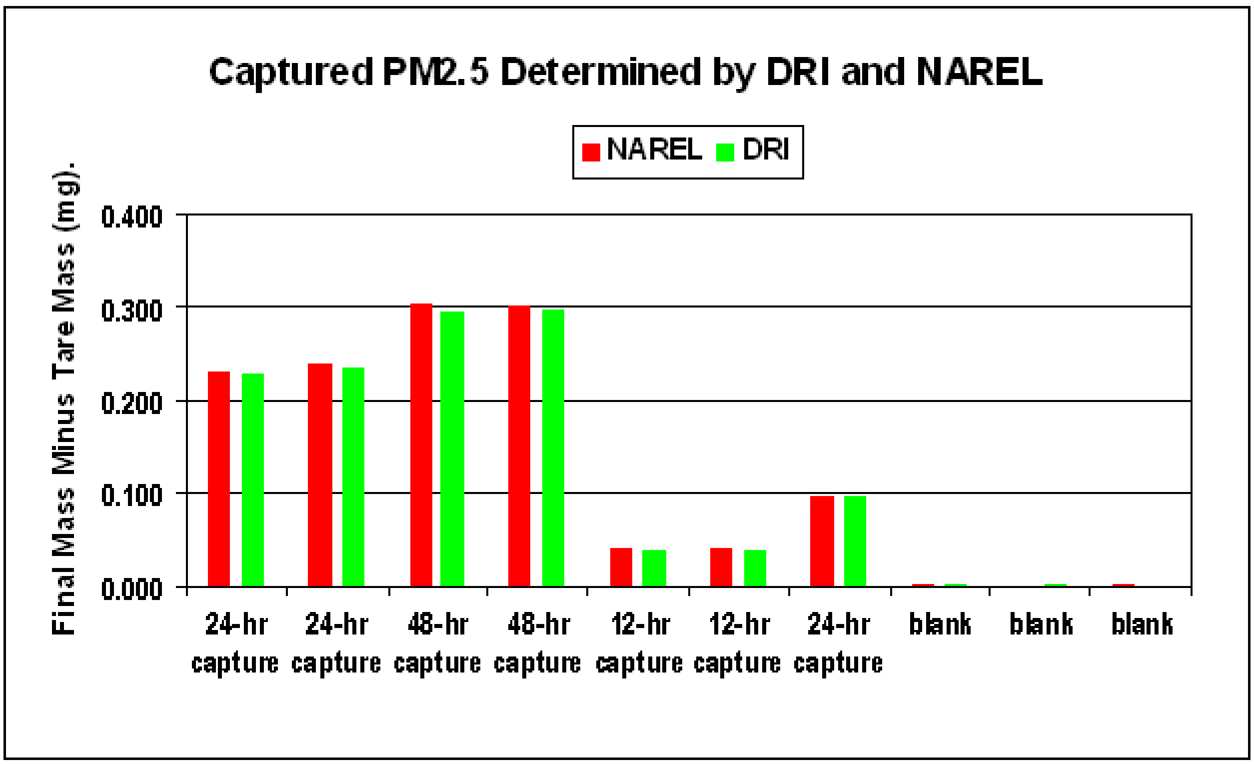

Figure 2

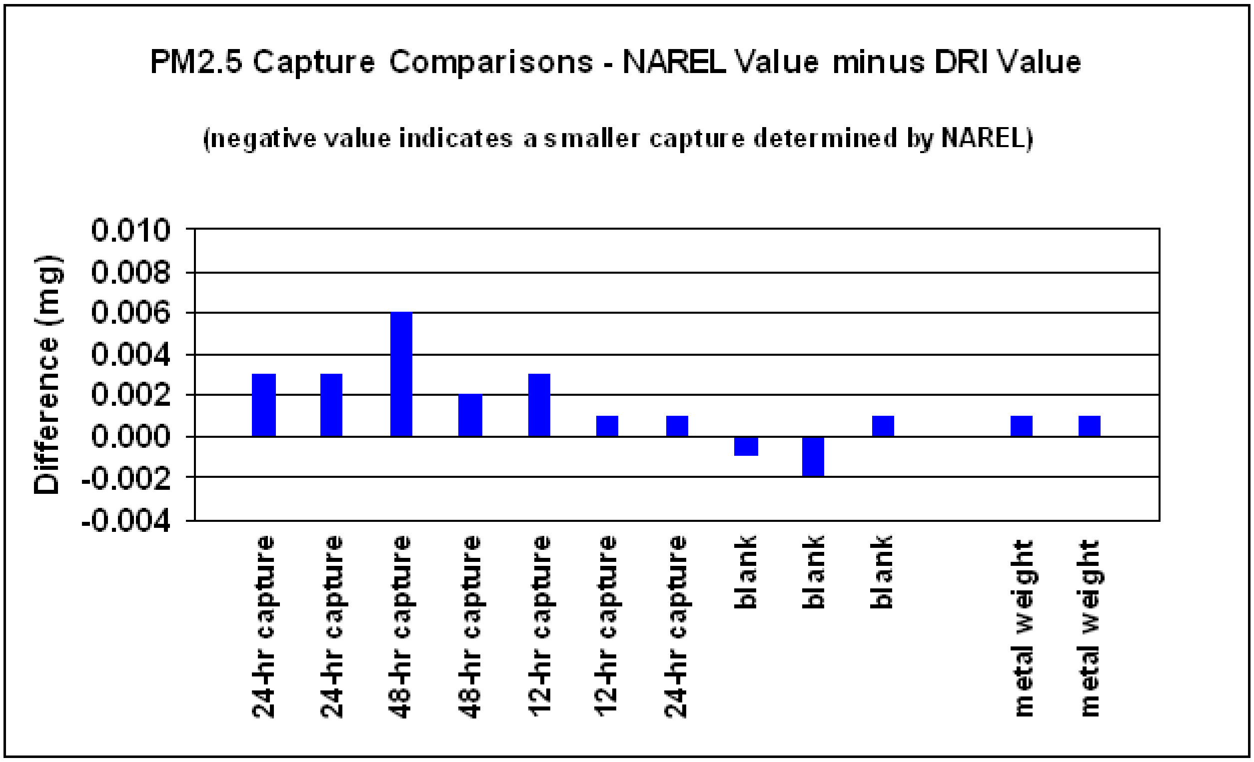

Figure 3

The TSA revealed well qualified personnel with good laboratory and quality control practices at DRI's gravimetric laboratory. The gravimetric laboratory follows or exceeds the guidelines listed in the EPA Quality Assurance Guidance Document 2.12. (Reference 4). No deficiencies for the gravimetric lab were noted. Overall good laboratory practices were observed during the TSA.

Ion Chromatography (IC) Laboratory

The IC analyses are performed by Ms. Barbara Hinsvark. She was interviewed for compliance to good laboratory practices, the QAPP, and the following SOPs.

- *DRI SOP #2-109.5 - Extraction of Ionic Species from Filter Samples* (Reference 6)
- *DRI SOP #2-203.5 - Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography* (Reference 7)
- *DRI SOP #2-208.1 - Cation Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography* (Reference 8)

The laboratory is equipped with an automated Dionex IC instrument. One channel is optimized for the analysis of anions and another channel is optimized for the analysis of cations. The lab also has equipment for cleaning and extracting Teflon®, Nylon®, and quartz filters. Ions are collected on Teflon® filters for the Texas samples. Gravimetric and XRF analyses must be performed and results validated before the Teflon® filters are extracted. Extractions are performed using an ultrasonic bath and a shaker table. The entire filter is placed into a 15 ml polystyrene tube and 200 µl of ethanol is added to the filter as a wetting agent. The extraction solvent for the Teflon® filters is nanopure deionized water.

Multilevel standards are used to develop calibration curves and establish retention times. New calibration curves are checked against a standard from a secondary source. Fresh curves are prepared weekly or when the routine check samples indicate excessive calibration drift. Ms. Hinsvark allowed the audit team to view a recent calibration curve and the associated quality control elements on the instrument's data system. No deficiencies were noted in reviewing the data.

Quality control elements practiced by the DRI IC laboratory include the following. Precision evaluation using results from duplicate filter analysis. Blank or matrix spikes are extracted along with field samples to evaluate method accuracy. Quality control samples (QCS) are analyzed as an independent check of the calibration standards. Continuing calibration blanks (CCB), continuing calibration verification (CCV) solutions, and lab blanks are also analyzed at a prescribed frequency to verify instrument and method performance.

The only specific samples discussed were those from the recent PE study conducted by NAREL. The Ion PE samples for the DRI study were created at NAREL using Met One SASS air samplers to collect replicate samples on Teflon® filter media. Although Nylon® is the standard filter material used for collection of ions for the STN network, ions collected for the Texas speciation network are currently being collected on the same Teflon® filter used for gravimetric and XRF analyses. A set of six Teflon® filters was sent to DRI for ion extraction and analysis and a replicate set of filters was extracted and analyzed at NAREL. Each set consisted of two blank filters, two replicate filters sampled on January 3, 2005, and two replicate filters sampled on January 4, 2005. A summary of the loaded filter PE results is shown in figure 4.

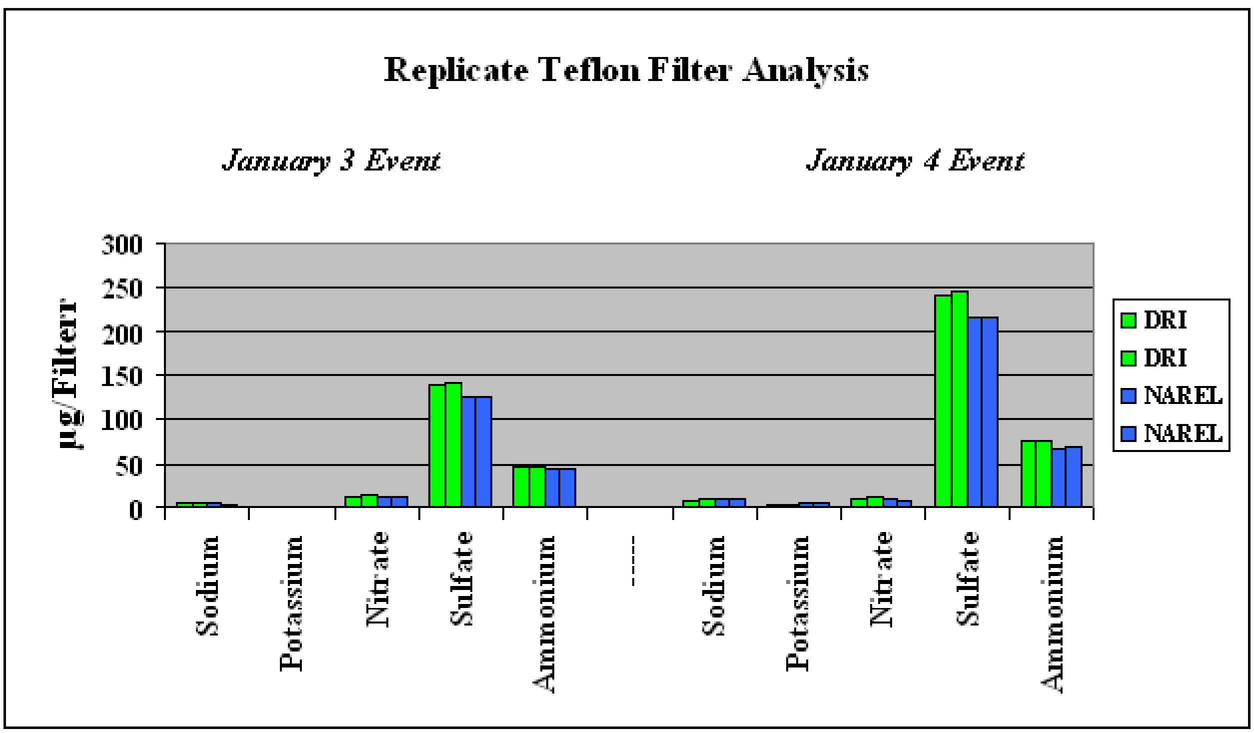

Figure 4

Although the results from the PE study indicated overall good performance from the IC laboratory, Dr. John Watson, DRI's Quality Assurance Manager, indicated that he would like to see better inter-laboratory agreement for the sulfate ion. Dr. Watson requested a set of NAREL's ion calibration solutions in order to compare instrument calibrations. In response to his request, NAREL has sent three aqueous solutions to DRI which include an ammonium sulfate standard, a five component anion standard, and a six component cation standard. Dr. Watson also requested to expand his participation in the PE study by analyzing a replicate set of the Nylon® filter PE samples that were analyzed by the three other participating laboratories. Analysis results of the loaded Nylon® filters are shown in Figure 5. A separate PE report including results from all participating laboratories will be available in the Summer of 2005 (Reference 1).

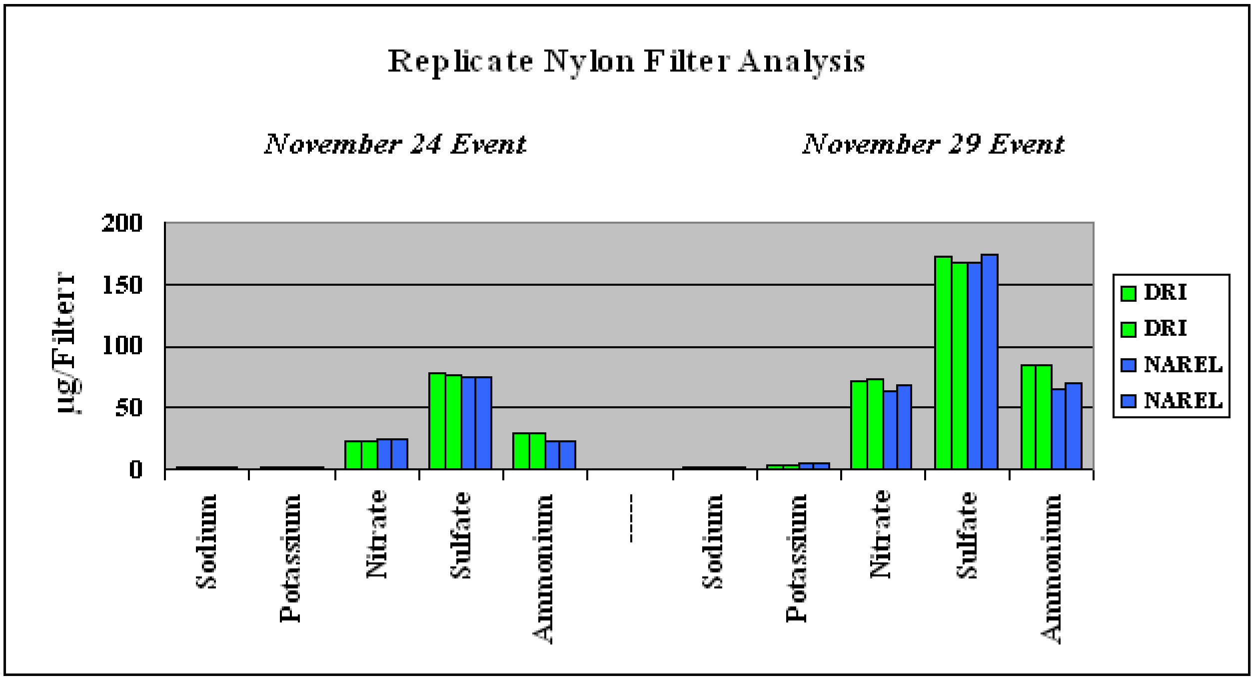

Figure 5

An issue with the R&P samplers used by Texas to collect speciation samples was a topic of discussion with Dr. Watson and Dr. Tropp. Specifically, use of this sampler could bias the TCEQ nitrate data. The R&P Model 2025 sequential sampler uses a Teflon® filter to collect samples for mass, elements, and ions analyses. The sequence of analyses for the Teflon® filter is gravimetric, XRF, and finally ions. The majority of monitoring sites in the National $PM_{2.5}$ speciation network use the Met One Sass sampler which has separate channels for Nylon®, Teflon®, and Quartz filters. Nylon® filters are used for collection of ions because of the affinity of Nylon® for nitrate compounds. Single channel speciation samplers such as the URG use a Nylon® filter behind the Teflon® filter as a backup to capture nitrates that may volatilize from the $PM_{2.5}$. The Met One and URG samplers also employ an acid denuder, such as magnesium carbonate, ahead of the filter to remove any nitric acid gas. The R&P 2025 does not use a denuder. One other concern in using the Teflon® filter for ion analysis is loss of sample during the preceeding XRF analysis. The Texas "test bed" studies using co-located samplers and alternate filter media are currently underway to determine the extent of bias and possible solutions.

Carbon Analysis Laboratory

The carbon analysis laboratory is supervised by Ms. Dana Trimble. Lab analyst Teresa Bohannan and Dr. Antony Chen were also present to answer questions about the carbon analysis and assist with the inspection of this laboratory to determine compliance with good laboratory practices, the QAPP, and the following SOPs.

- *DRI SOP #2-201.1 - DRI Model 2001 Thermal/Optical Carbon Analysis of Aerosol Filter Samples* (Reference 9)
- *DRI SOP #2-106.4 - Pre-firing and Acceptance Testing of Quartz-Fiber Filters for Aerosol and Carbonaceous Material Sampling* (Reference 10)

DRI has performed carbon analyses for the IMPROVE Program since the mid - 1980s using first generation model DRI/OGC thermal/optical carbon analyzers. Organic carbon (OC) compounds are thermally removed from a sub-sample (punch) of quartz filter sample using heating ramps of increasing temperature (550 ^{O}C maximum) and of *variable* duration while in a pure helium atmosphere. Elemental carbon (EC) is removed from the sample using additional temperature ramps (800 ^{O}C maximum) in a 98% helium/2% oxygen atmosphere. The thermally removed carbon compounds are converted to carbon dioxide (CO_2) and then to methane (CH_4) and measured using a flame ionization detector (FID). As the analysis progresses, each temperature stage results in a sub-fraction (OC1, OC2, OC3, OC4, EC1, EC2, and EC3) of the total carbon (TC) measured. Some OC compounds may be converted to EC due to incomplete combustion or pyrolysis during the helium stage of analysis. If not accounted for, the pyrolysis products (pyrolC) will bias the OC low and the EC high. To correct for this bias, an optical system consisting of a laser and photodetector continuously monitors the *reflectance* of the sample punch. Formation of pyrolysis products results in a decrease in reflectance from the reflectance determined at the beginning of the analysis. As the pyrolysis products are removed by oxidation, the reflectance increases. The point in time during the analysis when the reflectance reaches it's initial value is called the split point. All carbon evolved before the split point is assigned to OC with the remaining carbon assigned to EC. The portion of carbon that evolves from the beginning of the oxygen stage to the split point is reported as pyrolC. This carbon analysis method is known as the IMPROVE TOR Protocol.

Samples analyzed for the TCEQ contract require the STN Thermal Optical Transmittance (TOT) carbon method of analysis. The STN TOT carbon analysis method is based upon NIOSH method 5040 (Reference 11) which includes the determination of OC and EC, the sum of which represents the TC. EPA also requires reporting four fractions of the organic carbon and pyrolytic carbon: OC1, OC2, OC3, OC4, and PyrolC. The STN TOT method, in many ways similar to the IMPROVE method, thermally evolves OC from an aliquot of the quartz filter sample using *fixed* duration heating ramps (900 ^{O}C maximum) while in a pure helium atmosphere. EC is removed from the sample using additional fixed duration temperature ramps (920 ^{O}C maximum) in a 98% helium/2% oxygen atmosphere. In order to account for pyrolyzed carbon formed during the helium phase of analysis, *transmittance* of a laser through the quartz filter sample is monitored to determine when to begin attributing the detector signal to EC.

DRI/OGC analyzers are currently being replaced by the DRI Model 2001 analyzer. The new model has been redesigned to perform both the IMPROVE TOR OC/EC analysis method as well as an option to correct for pyrolysis with transmittance. A report issued by DRI in January, 2005 (Reference 12), details the procedures used to validate the Model 2001 instrument. Performance testing at DRI to compare analytical results between the old DRI/OGC model and the model 2001 instruments indicates satisfactory agreement with OC and EC results, however, agreement for carbon sub-fractions has not been satisfactory. The DRI report proposes two basic reasons for the poor sub-fraction agreement: (1) The sample oven temperature control of the DRI/OGC instrument is not as accurate and precise as in the new Model 2001. The DRI report presents data that shows the actual oven temperature of the DRI/OGC instrument is 10 - 50 ^{O}C higher than the indicated temperature. OC1, OC2, and EC2 were found to be most affected by temperature differences. (2) The DRI/OGC instrument unintentionally introduces small amounts of oxygen contamination into the system which results in premature oxidation of elemental carbon during the non-oxidizing helium stage of the protocol. DRI test results indicate that oxygen contamination has been reduced from approximately 250 parts per million (ppm) in the DRI/OGC to an average level of less than 25 ppm in the DRI 2001. PyroC, OC3, OC4, and EC1 are most affected by oxygen in the non-oxidizing stage of analysis. Minimization of oxygen contamination could be even more critical when performing the STN protocol because the higher temperature thermal profile (900 ^{O}C vs. 550 ^{O}C) increases the effects of the oxygen. A small quantity of oxygen contamination that may not cause significant removal of EC at 550 ^{O}C may be sufficient to oxidize significant amounts of EC at 900 ^{O}C.

In order for the Model 2001 instrument to maintain analytical consistency with the DRI/OGC instrument, a modification of the IMPROVE thermal profile was proposed by DRI. The new protocol, named IMPROVE_A, increases the set point of each temperature ramp by 20 - 40 ^{O}C. This allows the new instrument to operate at thermal conditions that are closer to the actual temperature conditions of the original DRI/OGC instrument. The IMPROVE_A protocol has recently been approved for the Model 2001 instrument by the IMPROVE steering committee. At the time of the audit, DRI had two Model 2001 instruments dedicated to STN method analysis of TCEQ samples and five Model 2001 instruments dedicated to IMPROVE samples.

Quality control measures in DRI's carbon laboratory are virtually identical for STN and IMPROVE samples. New quartz fiber filters are pre-fired to 900 ^{O}C for the STN network to remove possible carbon artifacts that could interfere with analysis. Acceptance testing of the pre-fired batch includes inspection of each filter for defects and carbon analysis of two filters from each batch of 100. Acceptance criteria for pre-fired quartz filters are OC < 1.5 $\mu g/cm^2$, EC < 0.5 $\mu g/cm^2$, and TC < 2.0 $\mu g/cm^2$ for the STN thermal protocol. The typical pre-fired STN quartz filter averages 0.56 $\mu g/cm^2$ TC.

Instrument calibration is performed using multiple levels of four different standards: two NIST traceable calibration gases and two spiking solutions. Multiple level calibrations are performed twice a year or when a new calibration gas is installed. Manual injection of calibration gases is performed as a daily QC check of instrument performance. Automatic injection of the methane calibration gas at the end of each analysis serves as an internal standard to normalize FID response.

Additional quality control elements practiced by the DRI carbon laboratory include the following: System blanks are analyzed weekly to check for contamination of the analyzers. Method detection limits (MDL) are determined from the analysis of lab blanks. The lower quantifiable Limits (LQL) are determined from the analysis of field blanks. Precision is evaluated using results from duplicate analyses at a rate of one per batch of ten (10% total). The duplicates are performed by analysts using an analyzer chosen at random from the ones originally used. Peak area of the calibration gas FID response is plotted on control charts and used to monitor instrument performance. Criteria for all QC measures are listed in the DRI Carbon SOP.

EPA has established data quality objectives for the $PM_{2.5}$ Speciation Network, and it is critical that all participating laboratories produce analytical results that are comparable with the national contract laboratory, Research Triangle Institute (RTI). The STN carbon analysis at RTI is virtually identical to the carbon analysis at NAREL. SOPs that describe the analysis at RTI and at NAREL are available for viewing on the web (Reference 13 and Reference 14). RTI and NAREL both use the carbon analyzer manufactured by Sunset Laboratories Inc. Although the DRI and the Sunset units are very similar, there are significant differences in both the hardware and the software. The current NAREL PE study, which includes carbon results from the DRI laboratory (Reference 1), indicates that these units can produce comparable data for OC and TC, however, reproducing STN method EC and OC sub-fractions appear to be the most challenging analyses for the DRI 2001 instrument.

A set of six quartz filter PE samples created at NAREL for STN carbon analysis were sent to DRI in January. Each set consisted of two blank filters, two replicate filters named April 27 Event and two replicate filters named November 16 Event. DRI volunteered to analyze the PE samples not only by the STN protocol but also by the original IMPROVE method and the new IMPROVE_A method. DRI analysts also performed duplicate analyses for each analysis method using different analyzers.

NAREL analyzed a replicate set of the PE samples by the STN method using a Sunset TOT analyzer. NAREL also analyzed the PE samples by the IMPROVE_A method using a second Sunset TOT/TOR analyzer that has been optimized for the IMPROVE_A TOR method. Figures 6 and 7 compare the IMPROVE_A analysis results from two DRI Model 2001 instruments and the NAREL Sunset TOT/TOR instrument. Very good inter-laboratory agreement of the OC/EC/TC is

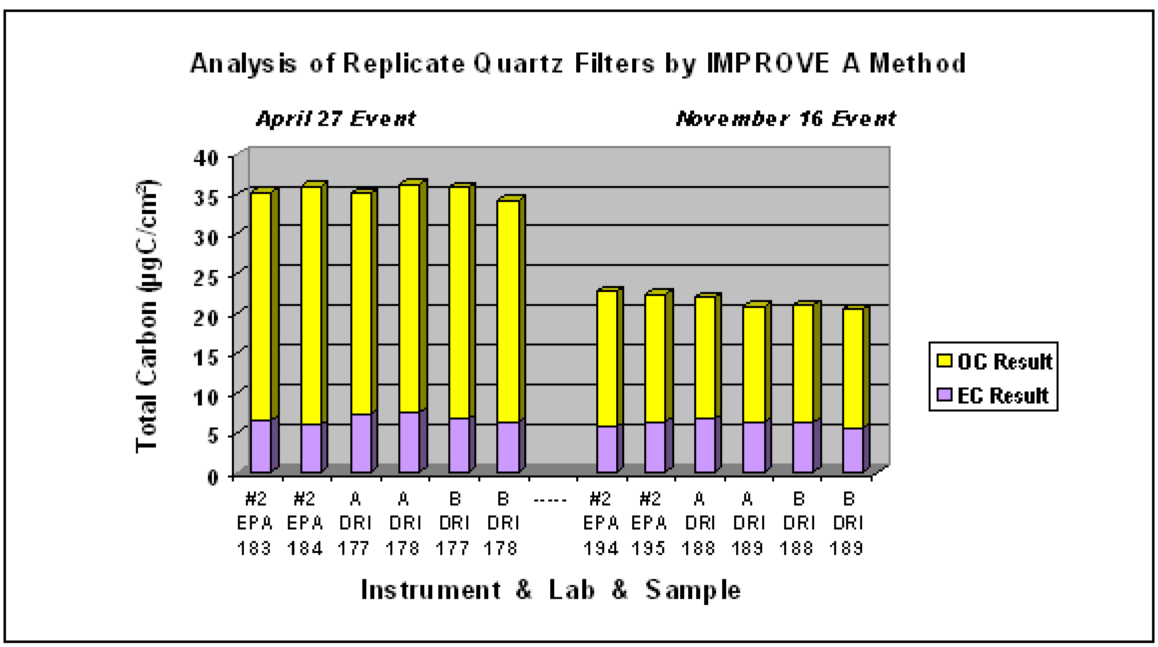

Figure 6

observed in figure 6 for the PE samples. Small discrepancies in TC may sometimes result from sample inhomogeneity.

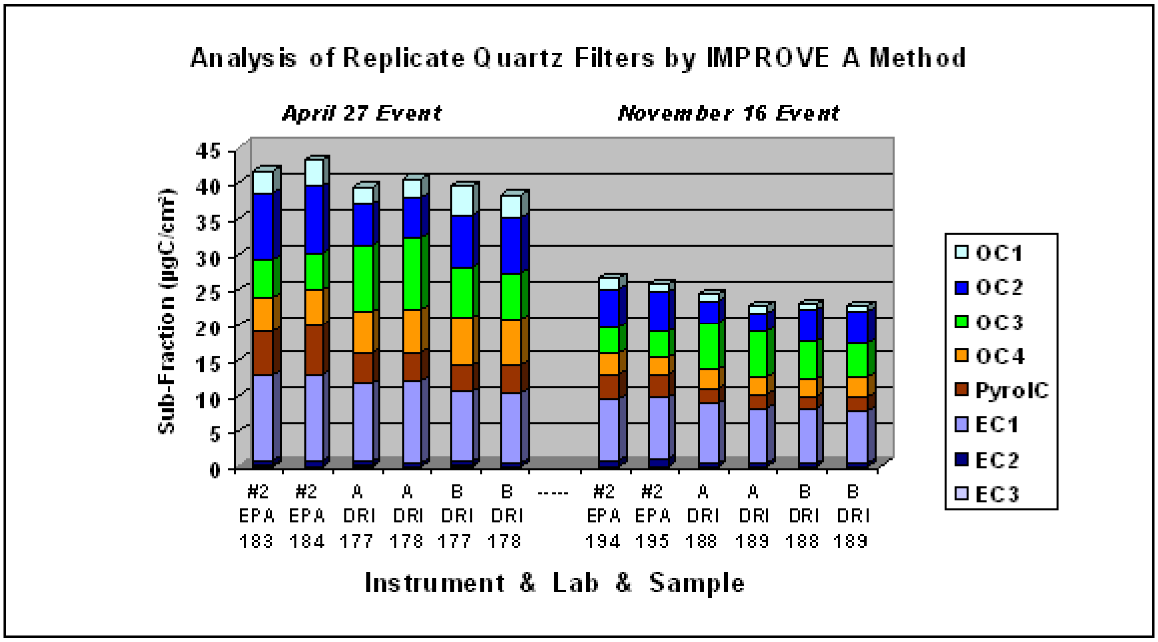

Figure 7

Figure 7 indicates relatively good sub-fraction agreement between the DRI 2001 and EPA Sunset TOT/TOR instruments.

Figures 8 and 9 compare the STN TOT analysis results from two DRI Model 2001 instruments and

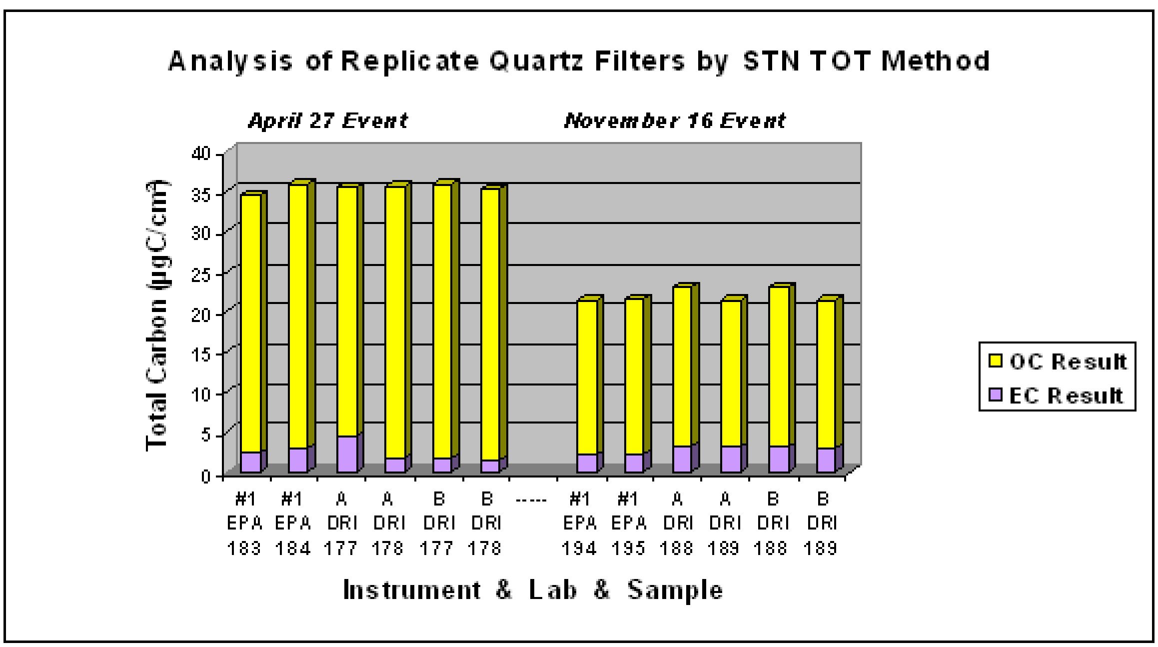

Figure 8

the NAREL Sunset TOT instrument. Although TC and OC show good agreement, figure 8 indicates that inter-laboratory agreement is not as good for EC determined by the STN analysis method. DRI analyzers determine higher EC for the November 16 event, but lower EC in 3 of 4 analyses for the April 27 event. Since only two samples were used, it is difficult to say whether this difference between DRI and NAREL EC is statistically significant.

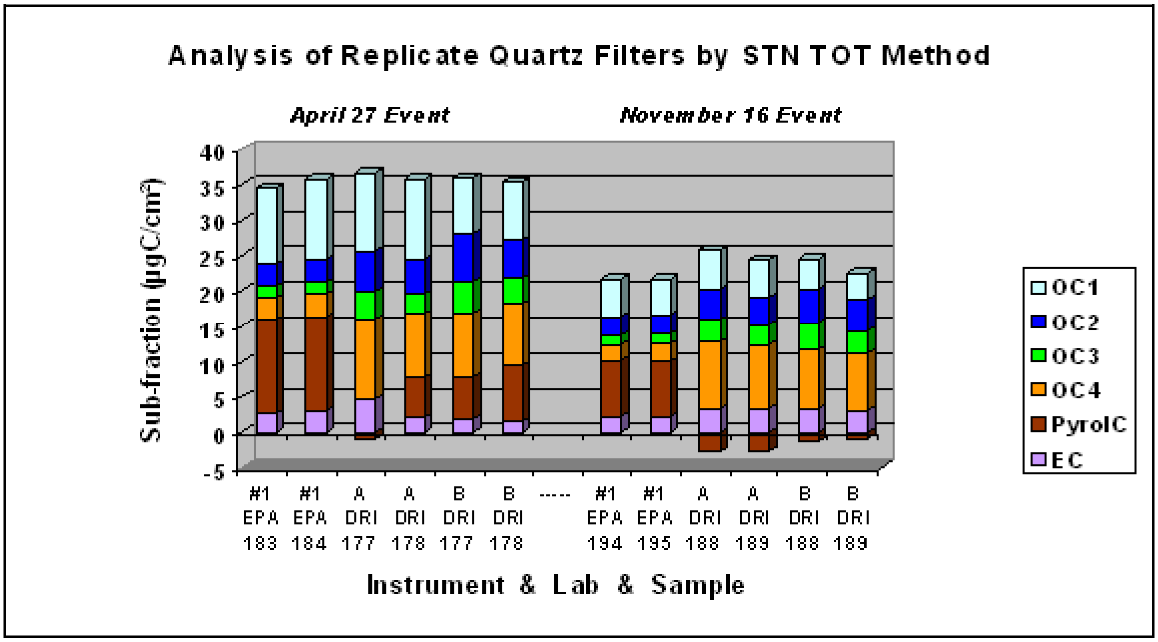

Figure 9

Figure 9 illustrates the difficulty in reproducing STN carbon sub-fractions. The OC4 and PyrolC sub-fractions show the greatest variability between the EPA and DRI instruments. The negative pyrolC shown in Figure 9 for some of the DRI STN analyses, indicates an early split point, that is, the split point between OC and EC was assigned by the instrument before the oxidizing stage of the analysis. Note: Negative pyrolC is a result of the method used by the DRI instrument software in dealing with an early split point. Although there were no early split points determined by the EPA Sunset instrument for the PE samples, if an analysis produces an early split point, the Sunset software reports zero pyrolC and ends the OC4 peak at the split point.

Allowing for an early split point, if indicated by the laser, is important because it is possible for a sample to contain certain elements that can catalyze the removal of EC before the oxidizing stage of analysis. With well characterized samples such as the PE samples, an early split point is an indication of oxygen contamination entering the system during the pure helium, non-oxidizing stage of analysis. The same samples analyzed by the IMPROVE_A method did not have early split points, possibly due to less oxygen contamination or the oxygen being less effective at removing EC at the lower temperatures generated with the IMPROVE protocol. It has been suggested that temperatures above 550 °C, even within a pure helium atmosphere, may cause pyrolyzed carbon to be removed from the filter segment, however, replicates of the same PE samples analyzed at NAREL show insignificant release of pyrolC using a 900-degree profile. Even with the STN protocol, OC/EC are more consistent than carbon fractions. With laser correction, OC and EC are less sensitive to the oxygen and temperature effects.

In addition to oxygen, other factors also contribute to between instrument variability for both the STN and IMPROVE methods. A few of the most significant factors are the following.

- Over or under estimation of the sample temperature during the analysis. At lower temperatures oxygen has very little or no affect on the sub-fractions. Differences in sample oven temperature calibration result in less OC1 and OC2 precision. This applies to both STN and IMPROVE methods. Higher temperature fractions (i.e., OC3 and OC4) are influenced by a combined effect of oxygen and temperature.
- Fixed duration thermal ramps specified by the STN method may not allow sufficient time for peak resolution. The rate of oven heating is more critical with the STN method because the fixed duration thermal ramps include the time it takes the temperature to reach the set point.
- Differences in criteria used to define the STN sub-fractions and differences in software algorithms used for peak identification will result in some variability. Sub-fraction criteria for the Sunset TOT instruments are determined experimentally from the analysis of sucrose and KHP standard solutions. Both the Sunset and the DRI 2001 analyzers rely on software algorithms to recognize peaks to determine when to advance to the next thermal ramp for IMPROVE analyses.

X-Ray Fluorescence Analysis

The elemental composition of particulate matter deposited on a Teflon® filter is determined by energy dispersive X-Ray Fluorescence (XRF). New Teflon® filters that are supplied by EPA for the $PM_{2.5}$ program have been subjected to numerous XRF analyses to determine background before the filter lots are accepted for distribution. The XRF analysis is performed after the gravimetric analysis has been completed.

The XRF laboratory is supervised by Mr. Steve Kohl. The primary instrument used for analysis of STN samples is a PANalytical Epsilon 5 energy dispersive XRF. Two Kevex Model 700 XRF analyzers serve as backup instruments. The PANalytical XRF utilizes a liquid nitrogen cooled germanium detector. Ten instrument conditions resulting in ten separate XRF analyses are conducted on each sample under vacuum. All 48 elements reported to AQS by RTI for the Speciation Trends Network are also reported by DRI for the TCEQ speciation samples. PE sample results were available for discussion and interviews and inspections were performed to determine compliance with good laboratory practices, the QAPP, and the following SOP.

- *DRI SOP #2-209.1 - X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (PANalytical Epsilon 5)* (Reference 17)

Instrument calibration is performed using thin film standards from Micromatter. Polymer film standards and NIST standards are used as calibration verification QC checks. A multi-element Micromatter standard is analyzed daily to check for instrument drift. A criteria of ±5% is used to determine if re-calibration is necessary. Energy calibration of the germanium detector is performed weekly using an automated program supplied with the operating software.

For each batch of samples analyzed, laboratory blanks are analyzed and the average concentration of each element is used for baseline correction. MDLs are determined quarterly from the analysis of a series of 24 Teflon® laboratory blanks. The MDL for each element is computed as 3 times the standard deviation of the element concentration. The lower quantifiable limits (LQL) are determined quarterly from the analysis of field blanks. The XRF measurement uncertainty of each element in a sample is calculated by adding the standard deviation of lab blank measurements to the absolute sample concentration multiplied by the relative standard deviation of multiple measurements of the low standard. Sample replicates are analyzed at a frequency of approximately one per ten samples. The criteria for re-analysis of previous samples is ±10% or three times the analytical uncertainty. No attenuation corrections are made for $PM_{2.5}$ samples. Control charts are maintained to monitor instrument performance.

Results of a recent PE study were discussed with laboratory personnel. The PE study consisted of replicate sets of Teflon® filter samples created at NAREL and distributed to four participating laboratories. The charts display elements only when each laboratory's result is greater than 3 times their measurement uncertainty. Figures 10 and 11 summarize the XRF results from the EPA and

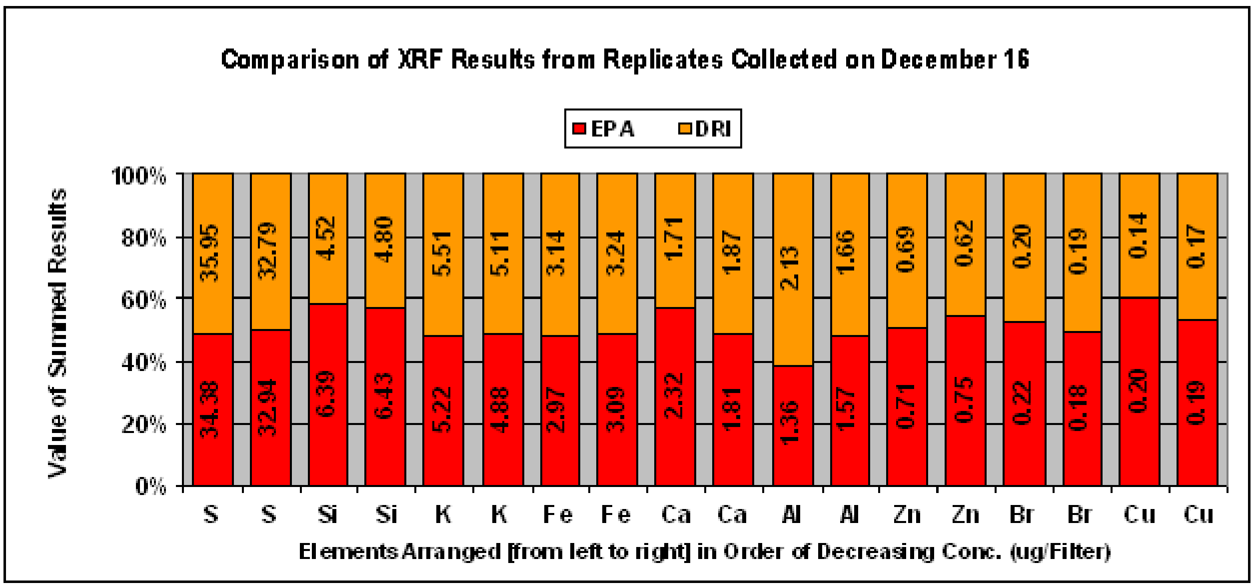

Figure 10

DRI laboratories. Each bar segment represents an individual value reported by an instrument. Elements are identified along the horizontal axis, and the elements are arranged from left to right in order of decreasing concentration. Although the measurement uncertainties are not included in this report, they are important in evaluating inter-laboratory comparisons. For example, a copper result illustrated in figure 11 appears to show poor inter-laboratory agreement (0.17 µg/filter versus 0.09 µg/filter or a relative difference of 63 %). However, DRI's reported concentration for this sample is only four times greater than the uncertainty of the measurement. When the measurement uncertainties are considered, figures 10 and 11 indicate relatively good inter-laboratory comparison for the PE samples.

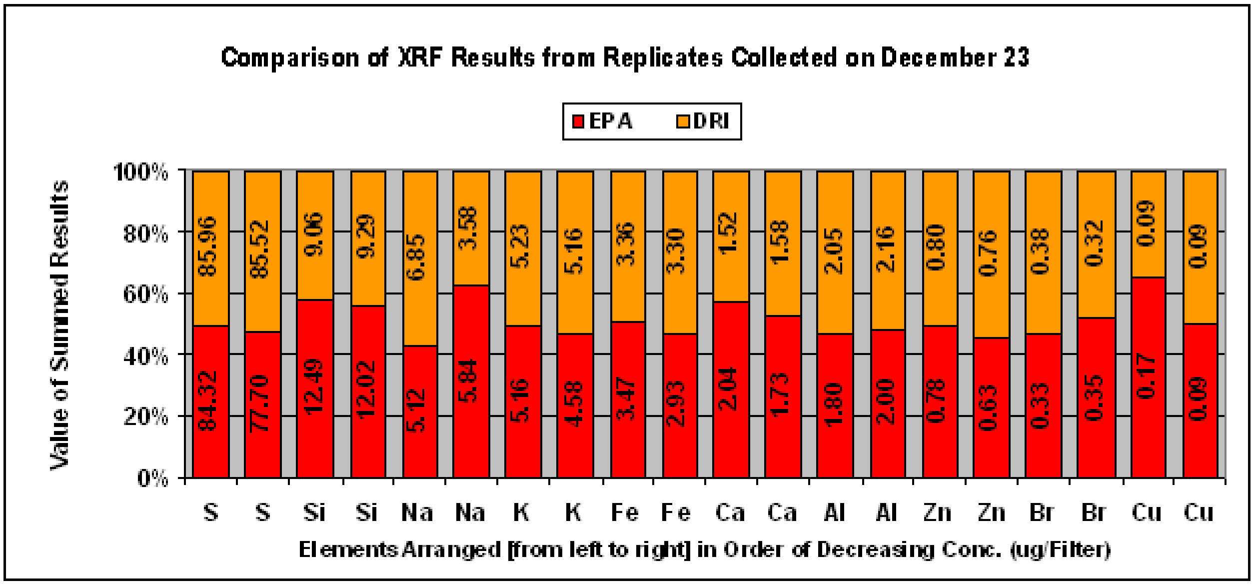

Figure 11

A suggestion was proposed by Dr. Watson to gather additional information from all laboratories participating in the PE study to document instrument parameters and analysis conditions used by each laboratory to generate XRF results. As a follow up, NAREL sent a questionnaire to each laboratory which includes a table for instrument conditions and MDLs and questions of how results were generated for the recent PE study. A comprehensive report of the PE study including the XRF questionnaire will be available in the summer of 2005 (Reference 1).

Good laboratory and quality control practices are performed in the XRF laboratory. No deficiencies were observed for the XRF laboratory during the TSA.

Data Processing, Validation, and Reporting

Due to time constraints, the audit team did not discuss in detail with DRI staff the specifics of their data management system. The following documents are available that describe DRI's data management and validation procedures for $PM_{2.5}$ Laboratory Support:

- *DRI SOP #3-004.2 - $PM_{2.5}$ FRM Data Processing and Data Validation* (Reference 18)
- *DRI SOP # 3-003.4 - Dry Deposition Field, Mass, and Chemical Data Processing and Data Validation.* (Reference 19)

The audit team was able to see how the sample information is acquired and entered into the laboratory information management system (LIMS) during the inspections of the various areas of the laboratory. Sample information may be acquired as hard copied data sheets or forms, data entered by keyboard into a computer file, or data retrieved directly from an instrument and transferred to an electronic database. The LIMS uses Microsoft Access for data entry and reporting combined with an SQL database programed to automate many data management tasks. There are documented procedures in place for making corrections to data at all stages of data processing and the database audit trail documents these edits.

DRI Support for Field Activities

In addition to the laboratory and logistical support described in this report, Dr. Richard Tropp, the TCEQ Project Manager, has provided on site training to TCEQ personnel to ensure a smooth transition from RTI to DRI laboratory support. An instruction document prepared by Dr. Tropp and Brenda Cristani for Texas field technicians is available for reference titled:

- *"Instructions for Filter Pack Identification, Completing Field Data Sheets, Shipping and Receiving Filters, and Obtaining Replacement Filters." [2004 Field Memo.doc]* (Reference 20)

This document emphasizes important changes to the procedures field technicians must perform to minimize loss of data during the transition to DRI laboratory support.

Conclusions

This TSA was conducted as part of the EPA required quality assurance oversight of two national air monitoring networks, the $PM_{2.5}$ Chemical Speciation Network and the IMPROVE Network. The DRI laboratory facility has recently begun laboratory support for the TCEQ $PM_{2.5}$ Chemical Speciation Network and has provided all carbon analyses for the IMPROVE Network since the program began. Observations made by the audit team on this initial inspection found the DRI Laboratory to be a modern facility with well qualified staff. DRI meets or exceeds compliance with good laboratory practices, the QAPP, and SOPs. No deficiencies were found in any of the inspected laboratory areas. Preliminary results of the recent PE study found good overall analytical agreement between NAREL and DRI. This audit has produced the following comments and recommendations.

- DRI QA documents such as their QAPP and SOPs are not currently available on the web.

  Recommendation: DRI QA documents should be posted on their web site or an EPA web site. (DRI management has already agreed to this recommendation.)

- This TSA revealed issues with the ion collection method used by TCEQ. The Texas R&P air samplers use Teflon® filters without a Nylon® filter backup to collect ions. DRI recognizes that a bias could exist in nitrate data collected by these samplers.

  Comment: Studies are being performed at DRI to determine the extent of bias and to find alternatives to the current ion collection method.

- The PE study results for carbon analysis were not available for review before the TSA and therefore the following was not discussed during the TSA. The DRI Model 2001 carbon analyzer using the modified IMPROVE_A Protocol has been approved by the IMPROVE Steering Committee. DRI studies have demonstrated that the new instrument is a much improved version with better temperature control and much lower oxygen levels in the pure helium stage than the previous DRI/OGC analyzer. The DRI Model 2001 compared well with NAREL's Sunset TOT/TOR analyzer when performing the IMPROVE_A method. Good inter-laboratory comparison was demonstrated for OC, EC, and TC as well as the sub-fractions. When performing the STN TOT method, good inter-laboratory agreement was seen for OC and TC, however agreement of EC and carbon sub-fraction results did not compare as well. Although there are several possible causes for the poor inter-laboratory agreement using the STN method, oxygen contamination of the DRI 2001 system during the non-oxidizing stage of analysis potentially has the greatest impact on the analysis. A small quantity of oxygen in helium that may not be detrimental for an IMPROVE protocol analysis may be sufficient to cause premature oxidation of EC when the higher temperature STN method is used. DRI already has procedures in place to minimize and monitor for oxygen in helium. NAREL has found that examination of thermograms generated from the analysis of sucrose spike solutions to be an effective way to check for premature oxidation.

The PE results described in this report are from a very small set of samples collected at one location to compare analytical results produced by different laboratories. The RTI/DRI inter-comparison data resulting from the Texas "test bed" study will provide additional valuable information in determining the comparability of the Sunset TOT and DRI 2001 instruments in performing the STN method.

Recommendation: DRI should continue their efforts to eliminate or at least reduce oxygen contamination of the Model 2001 instruments. Instruments performing the STN method should routinely analyze a sucrose standard solution as an additional check for excessive oxygen in helium.

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